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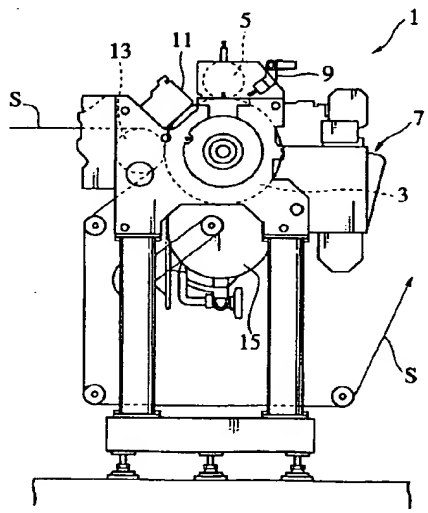
(54) Method and coating agent for electrocoagulation printing

(57) An improved electrocoagulation printing method comprises the steps of a) providing a positive electrode having a passivated surface moving at substantially constant speed along a predetermined path; b) coating the positive electrode surface with a coating agent containing silicon oxide and an oily substance to form on the surface micro-droplets of the coating agent; c) forming on the positive electrode surface having micro-droplets thereon a plurality of dots of coagulated ink representative of a desired image, by electrocoagulation of an electrolytically coagulable printing ink comprising an electrolytically coagulable polymer, a liquid medium, a soluble electrolyte and a coloring agent; and d-1) bringing a substrate into contact with the positive electrode surface to cause transfer of the dots of coagulated ink from the positive electrode surface onto the substrate and thereby imprint the substrate with the image.

The method prevents anode abrasion and pitting during electrocoagulation printing.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

[0001] The present invention pertains to improvements in the field of electrocoagulation printing. More particularly, the invention relates to a method of preventing anode abrasion and pitting during electrocoagulation printing.

[0002] In US Patent No. 4,895,629 of January 23, 1990, the inventor of the present application has described a high-speed electrocoagulation printing method and apparatus in which use is made of a positive electrode in the form of a revolving cylinder having a passivated surface onto which dots of coagulated ink representative of an image are produced. These dots of coagulated ink are thereafter contacted with a substrate such as paper to cause transfer of the coagulated ink onto the substrate and thereby imprint the substrate with the image. As explained in this patent, the positive electrode is coated with an oily substance prior to electrical energization of the negative electrodes in order to weaken the adherence of the dots of coagulated ink to the positive electrode. In addition, by using an olefinic substance as the oily substance, gas generated as a result of electrolysis upon energizing the negative electrodes is consumed by reaction with the olefinic substance so that there is no gas accumulation between the negative and positive electrodes.

[0003] The electrocoagulation printing ink which is injected into the gap defined between the positive and negative electrodes consists essentially of a solution or a dispersion comprising an electrolytically coagulable polymer, a liquid medium, a soluble electrolyte and a coloring agent. Where the coloring agent used is a pigment, a dispersing agent is added for uniformly dispersing the pigment into the ink. After coagulation of the ink, any remaining non-coagulated ink is removed from the surface of the positive electrode, for example, by scraping the surface with a soft rubber squeegee, so as to fully uncover the coagulated ink which is thereafter transferred onto the substrate. The surface of the positive electrode is thereafter cleaned by means of a plurality of rotating brushes and a cleaning liquid to remove any residual coagulated ink adhered to the surface of the positive electrode.

[0004] When a polychromic image is desired, the negative and positive electrodes, the positive electrode coating device, ink injector, rubber squeegee and positive electrode cleaning device are arranged to define a printing unit and several printing units each using a coloring agent of different color are disposed in tandem relation to produce several differently colored images of coagulated ink which are transferred at respective transfer stations onto the substrate in superimposed relation to provide the desired polychromic image. Alternatively, the printing units can be arranged around a single roller adapted to bring the substrate into contact with the dots of coagulated ink produced by each printing unit, and the substrate which is in the form of a continuous web is partially wrapped around the roller and passed through the respective transfer stations for being imprinted with the differently colored images in superimposed relation.

[0005] The inventor has observed that the metal oxide used in combination with the olefinic substance for coating the positive electrode causes abrasion and pitting of the positive electrode so that it is necessary to regrind the surface of such an electrode after every forty hours of printing. This of course requires shutdown of the printing apparatus and removal of the electrode. Where a positive electrode made of stainless steel or aluminum is utilized, Fe^{3+} or Al^{3+} ions are released from the surface of the electrode as a result of the abrasion and pitting thereof. As explained in the inventor's copending US application No. 08/376,245, these ions crosslink the electrolytically coagulable polymer contained in the ink, resulting in a viscosity increase leading to an ultimate gelation of the ink.

SUMMARY OF THE INVENTION

[0006] It is therefore an object of the present invention to overcome the above drawbacks and to provide a method of preventing anode abrasion and pitting during electrocoagulation printing.

[0007] In accordance with the present invention, there is thus provided an electrocoagulation printing method comprising the steps of:

a) providing a positive electrode having a passivated surface moving at substantially constant speed along a predetermined path;

b) coating the positive electrode surface with a coating agent containing silicon oxide and an oily substance to form on the surface micro-droplets of the coating agent;

c) forming on the positive electrode surface having micro-droplets thereon a plurality of dots of coagulated ink representative of a desired image, by electrocoagulation of an electrolytically coagulable printing ink comprising an electrolytically coagulable polymer, a liquid medium, a soluble electrolyte and a coloring agent; and

d-1) bringing a substrate into contact with the positive electrode surface to cause transfer of the dots of coagulated

ink from the positive electrode surface onto the substrate and thereby imprint the substrate with the image.

[0008] It has surprisingly been found, according to the invention, that by using the coating agent containing silicon oxide and an oily substance, one eliminates the abrasion and pitting of the positive electrode, without substantially affecting passivation, so that the requirement to regrind the surface of the positive electrode is significantly reduced. Moreover, since there is no longer any release of contaminant ions from the surface of the positive electrode due to abrasion and pitting thereof, the ink is stable and does not undergo an undesirable increase in viscosity during electrocoagulation printing. Thus, there is no longer any need to utilize two separate inks, that is, a starting ink and a replenishing ink having different concentrations of sequestering agent, as proposed in the aforementioned US application No. 08/376,245, and one may use only the starting ink which contains a sequestering agent for complexing other contaminant ions.

[0009] Where a polychromic image is desired, steps (b), (c) and (d-1) of the above electrocoagulation printing method are repeated several times to define a corresponding number of printing stages arranged at predetermined locations along the aforesaid path and each using a coloring agent of different color, and to thereby produce several differently colored images of coagulated ink which are transferred at the respective transfer positions onto the substrate in superimposed relation to provide a polychromic image. It is also possible to repeat several times steps (a) through (d-1) to define a corresponding number of printing stages arranged in tandem relation and each using a coloring agent of different color, and to thereby produce several differently colored images of coagulated ink which are transferred at respective transfer positions onto the substrate in superimposed relation to provide a polychromic image, the substrate being in the form of a continuous web which is passed through the respective transfer positions for being imprinted with the colored images at the printing stages. Alternatively, the printing stages defined by repeating several times steps (a) through (d-1) can be arranged around a single roller adapted to bring the substrate into contact with the dots of coagulated ink of each printing stage and the substrate which is in the form of a continuous web is partially wrapped around the roller and passed through the respective transfer positions for being imprinted with the colored images at the printing stages. The last two arrangements are described in the inventor's US Patent No. 4,895,629.

[0010] When a polychromic image of high definition is desired, it is preferable to bring an endless non-extendible belt moving at substantially the same speed as the positive electrode and having on one side thereof a coagulated ink retaining surface adapted to releasably retain dots of coagulated ink to cause transfer of the differently colored images at the respective transfer positions onto the coagulated ink retaining surface of such a belt in superimposed relation to provide a polychromic image, and thereafter bring the substrate into contact with the coagulated ink retaining surface of the belt to cause transfer of the polychromic image from the coagulated ink retaining surface onto the substrate and to thereby imprint the substrate with the polychromic image.

[0011] As explained in a copending US patent application in the name of the inventor, filed concurrently with the present application, by utilizing an endless non-extendible belt having a coagulated ink retaining surface such as a porous surface on which dots of coagulated ink can be transferred and by moving such a belt from one printing unit to another, so that the coagulated ink retaining surface of the belt contacts the coagulated ink in sequence, it is possible to prevent the paper web from being displaced between the positive electrode and the pressure rollers in a direction parallel to the longitudinal axis of the positive electrode, and to significantly improve the registration of the differently colored images upon their transfer onto the coagulated ink retaining surface of the belt, thereby providing a polychromic image of high definition which can thereafter be transferred onto the paper web or other substrate and in which the differently colored images are perfectly superimposed. For example, use can be made of a belt comprising a plastic material having a porous coating of silica.

[0012] Accordingly, the present invention also provides, in another aspect thereof, a multicolor electrocoagulation printing method comprising the steps of:

a) providing a positive electrode having a passivated surface moving at substantially constant speed along a predetermined path;

b) coating the positive electrode surface with a coating agent containing silicon oxide and an oily substance to form on the surface micro-droplets of the coating agent;

c) forming on the positive electrode surface having micro-droplets thereon a plurality of dots of coagulated ink representative of a desired image, by electrocoagulation of an electrolytically coagulable printing ink comprising an electrolytically coagulable polymer, a liquid medium, a soluble electrolyte and a coloring agent;

d-2) bringing an endless non-extendible belt moving at substantially the same speed as the positive electrode and having on one side thereof a coagulated ink retaining surface adapted to releasably retain dots of electrocoagulated ink, into contact with the positive electrode surface to cause transfer of the dots of coagulated ink from the

positive electrode surface onto the coagulated ink retaining surface of the belt and to thereby imprint the coagulated ink retaining surface with the image;

e) repeating steps (b), (c) and (d-2) several times to define a corresponding number of printing stages arranged at predetermined locations along the path and each using a coloring agent of different color, and to thereby produce several differently colored images of coagulated ink which are transferred at respective transfer positions onto the coagulated ink retaining surface in superimposed relation to provide a polychromic image; and

f) bringing a substrate into contact with the coagulated ink retaining surface of the belt to cause transfer of the polychromic image from the coagulated ink retaining surface onto the substrate and to thereby imprint the substrate with the polychromic image.

[0013] The invention provides a coating agent to be used in coating a positive electrode surface in advance of forming on the positive electrode surface a plurality of dots of coagulated ink by electrocoagulation of an electrolytically coagulable printing ink, the coating agent containing silicon oxide and an oily substance. The silicon oxide may be silicon dioxide. The oily substance may be an olefinic compound, such as unsaturated fatty acid selected from the group consisting of arachidonic acid, linoleic acid, linolenic acid, oleic acid and palmitoleic acid.

BRIEF DESCRIPTION OF THE DRAWING

[0014]

Figure 1 shows a schematic illustration of an electrocoagulation printing apparatus for carrying out the method of the present invention.

Figure 2 shows an enlarged schematic illustration of a printing unit of an electrocoagulation printing apparatus, explaining the steps of the method of the present invention.

Figure 3 shows a schematic illustration of a multicolor electrocoagulation printing apparatus for carrying out the method of the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0015] The coating agent according to this invention contains silicon oxide and an oily substance. The silicon oxide can be silicon dioxide (silica). The use of hydrophilic silicon dioxide may be preferable. Still more, it is preferable for the silicon dioxide to have a BET surface area of from about 100 to about 600 m^2/g. For example, a product sold by Degussa AG under the trade name of FK500LS having a BET surface area of about 450 m^2/g can preferably be used. The silicon dioxide is preferably used in an amount of from about 2 to about 40% by weight, or more preferably, in an amount of from about 5 to about 30% by weight, based on the total weight of the coating agent.

[0016] The oily substance can be fatty acids, higher alcohols, ester compounds of fatty acids. Preferably the oily substance is a non-volatile compound. A coating agent containing a volatile oily substance tends to change in the composition thereof as the printing time passes. Any such oily substance can be used singly or in combination.

[0017] Examples of fatty acids include unsaturated fatty acids such as arachidonic acid, linoleic acid, linolenic acid, oleic acid, palmitoleic acid and myristoleic acid, and saturated fatty acids such as caprylic acid, pelargonicacid, capricacid, lauric acid, isostearic acid, myristic acid and stearic acid. Examples of higher alcohols include octyl alcohol, decyl alcohol, lauryl alcohol, myristyl alcohol, oleyl alcohol, isostearyl alcohol, 2-hexadecyl alcohol and 2-octyldodecyl alcohol. Given as examples of the ester compounds of fatty acids are unsaturated or saturated monoesters, diesters and triesters.

[0018] Examples of monoesters include: monoesters of unsaturated fatty acids such as methyl oleate, ethyl oleate, propyl oleate, butyl oleate, isobutyl oleate, octyl oleate, isooctyl oleate, lauryl oleate, oleyl oleate, 2-ethylhexyl oleate, methyl linoleate, methyl linolenate and methyl ricinoleate; monoesters of saturated fatty acids such as methyl caprylate, methyl caproate, methyl enanthate, methyl pelargonate, methyl caprate, methyl undecanoate, methyl laurate, methyl tridecanoate, methyl myristate, methyl pentadecanoate, cetyl 2-ethylhexanoate, isopropyl myristate, octyldodecyl myristate, 2-ethylhexyl stearate and isononyl isononanate. Monoesters derived from natural fats and oils are also used to reduce the production cost. Examples of such a monoester include palm kernel oil methyl ester, coconut oil methyl ester, palm oil methyl ester, beef tallow fatty acid methyl ester, rapeseed oil methyl ester and rapeseed butyl ester. Examples of diesters include dibutoxyethyl sebacate and neopentyl glycol dicaprate. Examples of triesters include: triesters of unsaturated vegetable oils such as corn oil, linseed oil, olive oil, peanut oil, bean oil, sunflower oil, safflower

oil, palm oil, palm kernel oil, coconut oil and castor oil; triglycerides of unsaturated fatty acids such as oleic acid, linoleic acid and linolenc acid; triglycerides of saturated fatty acids such as seridocaprylic acid, capric acid and myristic acid.

[0019] The use of olefinic substances containing at least one double bond is preferable, then gas generated as a result of electrolysis upon energizing the negative electrodes is consumed by reaction with the olefinic substance so that there is no gas accumulation between the negative and positive electrodes. Particularly, unsaturated fatty acid selected from the group consisting of arachidonic acid, linoleic acid, linolenic acid, oleic acid and palmitoleic acid can be preferably used.

[0020] A coating agent containing silicon dioxide as silicon oxide and unsaturated fatty acid as an oily substance is preferably used. A preferred coating agent contains form about 5 to about 10% by weight of silicon dioxide and from about 90 to about 95% by weight of unsaturated fatty acid, or more preferably, about 7.5% by weight of silicon dioxide and about 92.5% by weight of unsaturated fatty acid so as to achieve the desired action of the coating agent while keeping suitable viscosity thereof.

[0021] The coating agent of the present invention may further contain a nonionic surfactant having a chain of polyethylene oxide (CH_2CH_2O), which has an effect on softening of the dots of coagulated ink, to weaken the adhesion of the dots of coagulated ink to the positive electrode. The types and amount of the surfactant are preferably determined so as to impart an appropriate hardness to the dots of coagulated ink. Specifically, the amount of the surfactant is preferably from about 5 to about 50% by weight, or more preferably, from about 10 to about 40% weight. Examples of the surfactants include polyoxyethylene lauryl ether, polyoxyethylene oleyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, polyoxyethylene sorbitanoleic acid ester, polyoxyethylene tetraoleic acid sorbitol and polyoxyethylene polydimethylsiloxane. The coating agent may also contain unsaturated vegetable wax such as carnauba wax to adjust the viscosity as well as to increase the lubricating property of the coating agent.

[0022] The coating agent of the present invention can be produced only by mixing with stirring using a mixer or by using a dispersing machine to micronize silicon oxide further. As a dispersing machine, generally used one such as roller mill, ball mill, pebble mill, attritor, or sand mill may be adopted. A coating agent containing silicon dioxide with a desired particle size distribution can be produced by appropriately controlling the dispersing condition, for example, a size of milling media used in a dispersing machine, packing density of the milling media, dispersion treating time and discharge rate. Unexpected bulky particles mixed in the coating agent of the present invention may prevent the electrocoagulation of printing ink comprising an electrolytically coagulable polymer, thereby to lower the image quality. It is therefore desirable to remove the bulky particles and the like by filtration or the like. As a filter, a gravitational, vacuum, pressure or centrifugal filter, or any conventionally known apparatus may be used.

[0023] The coating agent of the present invention which is produced by the aforementioned method is preferably a liquid under the usual operating condition, or more specifically, at the temperature range of from about 20 to about 60°C. There is a tendency to accompany difficulty in coating uniformly the positive electrode surface with a coating agent having a form other than a liquid. For example, when the coating agent of the present invention is a solid, a means is required to heat a means of applying the coating agent and/or the positive electrode surface. The viscosity of the coating agent is preferably from about 100 to about 100,000 cps, or more preferably, from about 1,000 to about 30,000 cps at 30°C. The viscosity of the coating agent can be appropriately controlled by changing the types and amount of the aforementioned silicon oxide and oily substance. In addition, a coating agent with high viscosity can be obtained by using either an oil-soluble thickener produced by modifying dextrin or an oil-soluble resin such as ethyl cellulose.

[0024] An electrolytically coagulable printing ink according to this invention contains at least an electrolytically coagulable polymer, a liquid medium, a soluble electrolyte and a coloring agent. As an electrolytically coagulable polymer, use can be made of a linear high molecular weight compound, that is , a polymer having a weight average molecular weight between about 10,000 and about 1,000,000, preferably between about 100,000 and about 600,000.

[0025] Moreover, the electrolytically coagulable polymer suitably contains a reaction site which includes a functional group selected from the group consisting of an amino group, an amide group and a carboxyl group. The reaction site makes a chemical bond with the multivalent metallic ion produced from the positive electrode, especially a trivalent ion such as ferric ion and aluminum ion, to thereby cause an electrocoagulation of the ink.

[0026] Examples of suitable polymers include natural polymers such as albumin, gelatin, casein and agar, and synthetic polymers such as polyacrylic acid and polyacrylamide. A particularly preferred polymer is an anionic copolymer of acrylamide and acrylic acid having a weight average molecular weight of about 250,000 and sold by Cyanamid Inc. under the trade mark ACCOSTRENGTH 86.

[0027] The polymer used can be in a liquid form either solution or dispersion which includes colloid, etc. The polymer can preferably be used in an amount of from about 6.5 to about 12% by weight, or more preferably, in an amount of from about 7 to about 10% by weight, based on the total weight of the ink, so as to provide suitable tone of dots of coagulated ink while keeping suitable viscosity of the coating agent. Water can preferably be used as a liquid medium for dispersing or dissolving the polymer to provide the desired electrolytically coagulable printing ink.

[0028] Preferred soluble electrolytes include alkali metal halides such as lithium chloride, sodium chloride and potassium chloride, and alkaline earth metal halides such as calcium chloride. Potassium chloride is particularly preferred.

The soluble electrolyte can preferably be used in an amount of from about 4.5 to about 10% by weight based on the total weight of the ink, when operating at a temperature ranging from about 35 to about 60°C.

[0029] The coloring agent can be a dye or a pigment. Examples of suitable dyes are water soluble dyes, include indigo dye, azo dye, anthraquinone dye, fluoran dye, dioxazine dye, oxazine dye and phthalocyanine dye. Examples of suitable pigments include organic pigments such as azo pigment, phthalocyanine pigment, quinacridone pigment, anthraquinone pigment, dioxazine pigment, thioindigo pigment, perynone pigment, perylene pigment, isoindolinon pigment and azomethine pigment, and inorganic pigments such as carbon black. A dispersing agent may be added for uniformly dispersing the pigment into the ink. Preferred dispersing agents include an anionic dispersing agent; a metal salt of naphtalenesulfonic acid-formaldehyde condensation product. The pigment can preferably be used in an amount of from about 6.5 to about 15% by weight, and the dispersing agent in an amount of from about 0.1 to about 6.0% by weight, based on the total weight of the ink.

[0030] The positive electrode used can be in the form of a moving endless belt as described in the inventor's US Patent No. 4,661,222, or in the form of a revolving cylinder as described in the aforementioned US Patent Nos. 4,895,629 and 5,538,601, the teachings of which are incorporated herein by reference.

[0031] Referring now to Fig. 1, there is illustrated an embodiment of an electrocoagulation printing apparatus for carrying out the method of the present invention. This apparatus 1 comprises a positive electrode 3 made of stainless steel, a plurality of negative electrodes 5 having a diameter of 50 μm and spaced from the positive electrode 3 by a constant predetermined gap, a coating unit 7 for coating the positive electrode surface with a coating agent to form micro-droplets thereof on the positive electrode surface, an ink discharge unit 9 for supplying electrocoagulation printing ink to the positive electrode 3, a removing unit 11 using a soft polyurethane squeegee for removing non-coagulated ink from the positive electrode surface, a transferring unit 13 using a pressure roller formed of polyurethane for transferring the dots of coagulated ink onto the substrate from the positive electrode surface, and a cleaning unit 15 for cleaning the positive electrode surface by jetting a cleaning liquid thereagainst. As shown in Fig. 1, when using a positive electrode in the form of the revolving cylindrical positive electrode, the printing steps (b), (c) and (d-1) are arranged around the positive cylindrical electrode. Figure 2 shows an enlarged schematic illustration of a printing unit of an electrocoagulation printing apparatus, explaining the method of the steps of the present invention, in which parts similar to those previously described with reference to Fig. 1 are denoted by the same reference numerals.

[0032] Preferably, the positive electrode surface and the ink are maintained at a temperature of about 35-60°C, or more preferably about 40°C, to increase electric conductivity of the ink in step (c) and a release of metal ions from the positive electrode surface into ink, thereby the metal ions are released in a quantity sufficient to increase optical density of the coagulated ink, and a coagulation efficiency in step (c) is increased.

[0033] The coating agent of the invention is advantageously applied onto the positive electrode surface by providing a distribution roller extending parallel to the positive cylindrical electrode and having a peripheral coating comprising an oxide ceramic material, applying the coating agent onto the ceramic coating to form on a surface thereof a film of the coating agent uniformly covering the surface of the ceramic coating, the film of coating agent breaking down into micro-droplets having substantially uniform size and distribution, and transferring the micro-droplets from the ceramic coating onto the positive electrode surface. As explained in inventor's US Patent No. 5,449,392 of September 12, 1995, the teaching of which is incorporated herein by reference, the use of a distribution roller having a ceramic coating comprising an oxide ceramic material enables one to form on a surface of such a coating a film of the coating agent which uniformly covers the surface of the ceramic coating and thereafter breaks down into micro-droplets having substantially uniform size and distribution. The micro-droplets formed on the surface of the ceramic coating and transferred onto the positive electrode surface generally have a size ranging from about 1 to about 5 μ. A particularly preferred oxide ceramic material forming the aforesaid ceramic coating comprises a fused mixture of alumina and titania. Such a mixture can comprise form about 60 to about 90% by weight of alumina and from about 10 to 40% by weight of titania.

[0034] According to a preferred embodiment of the invention, as shown in Fig. 2, the coating agent is applied onto the ceramic coating by disposing an applicator roller 73 parallel to the distribution roller 71 and in pressure contact engagement therewith to form a first nip 72, and rotating the applicator roller 73 and the distribution roller 71 in register while feeding the coating agent into the first nip 72 by using a ink feeding device 77, whereby the coating agent upon passing through the first nip 72 forms a film uniformly covering the surface of the ceramic coating. The micro-droplets are advantageously transferred from the distribution roller 71 to the positive electrode 3 by disposing a transfer roller 75 parallel to the distribution roller 71 and in contact engagement therewith to form a second nip 74, positioning the transfer roller 75 in pressure contact engagement with the positive electrode 3 to form a third nip 76, and rotating the transfer roller 75 and the positive electrode 3 in register for transferring the micro-droplets from the distribution roller 71 to the transfer roller 75 at the second nip 74 and thereafter transferring the micro-droplets from the transfer roller 75 to the positive electrode 3 at the third nip 76. Such an arrangement of rollers is described in the aforementioned US Patent No. 5,449,392.

[0035] Preferably, the applicator roller and the transfer roller are each provided with a peripheral covering of a resilient material which is resistant to attack by the coating agent, such as a synthetic rubber material. For example, use can be

made of a polyurethane having a Shore A hardness of from about 50 to about 70 in the case of the applicator roller, or a Shore A hardness of from about 60 to about 80 in the case of the transfer roller.

[0036] When use is made of a positive electrode of cylindrical configuration rotating at substantially constant speed about its central longitudinal axis, step (c) of the above electrocoagulation printing method is carried out by:

i) providing a plurality of negative electrodes 5 electrically insulated from one another and arranged in rectilinear alignment to define a series of corresponding negative electrode surfaces disposed in a plane parallel to the longitudinal axis of the positive electrode 3 and spaced from the positive electrode surface by a constant predetermined gap 6, the negative electrodes being spaced from one another by a distance at least equal to the electrode gap 6;

ii) filling the electrode gap 6 with the aforesaid electrocoagulation printing ink;

iii) electrically energizing selected ones of the negative electrodes to cause point-by-point selective coagulation and adherence of the ink onto the coated positive electrode surface opposite the electrode surfaces of the energized negative electrodes while the positive electrode is rotating, thereby forming the dots of coagulated ink; and

iv) removing any remaining non-coagulated ink from the positive electrode surface.

[0037] As explained in US Patent No. 4,895,629, spacing of the negative electrodes from one another by a distance which is equal to or greater than the electrode gap prevents the negative electrodes from undergoing edge corrosion. On the other hand, coating of the positive electrode with the coating agent of this invention prior to electrical energization of the negative electrodes weakens the adherence of the dots of coagulated ink to the positive electrode and also prevents an uncontrolled corrosion and pitting of the positive electrode.

[0038] Examples of suitable metals from which the positive and negative electrodes can be made are stainless steel, platinum, chromium, nickel and aluminum. The positive electrode is preferably made of stainless steel, tin or aluminum so that upon electrical energization of the negative electrodes, dissolution of the passive oxide film on such an electrode generates metallic ions, especially multivalent ions, which then initiate coagulation of the ink. Particularly, trivalent ions such as ferric ion and aluminum ion are suitable for causing coagulation of the ink.

[0039] The gap which is defined between the positive and negative electrodes can range from about 50 μm to about 100 μm, the smaller the electrode gap the sharper are the dots of coagulated ink produced. Where the electrode gap is of the order of 50 μm, the negative electrodes are preferably spaced from one another by a distance of about 75 μm.

[0040] The positive electrode surface coated with the coating agent is preferable polished to increase the adherence of the micro-droplets onto the positive electrode surface, prior to step (c) (ii). For example, as shown in Fig. 2, use can be made of a rotating brush 8 provided with a plurality of radially extending bristles 81 made of horsehair and having extremities contacting the surface of the positive electrode 3. The friction caused by the bristles 81 contacting the surface of the positive electrode 3 upon rotation of the brush 8 has been found to increase the adherence of the micro-droplets onto the positive electrode surface.

[0041] The step (c) (ii) of the above electrocoagulation printing method is advantageously carried out by continuously discharging the ink onto the positive electrode surface 3 from an ink discharge unit 9 disposed adjacent the electrode gap 6 and allowing the ink to flow along the positive electrode surface, the ink being thus carried by the positive electrode 3 upon rotation thereof to the electrode gap 6 to fill same.

[0042] After coagulation of the ink, any remaining non-coagulated ink is advantageously removed from the positive electrode surface, for example, the step (c) (iv) is carried out by scraping the surface with a soft rubber squeegee 11, as shown in Fig. 2, so as to fully uncover the coagulated ink. Preferably, the non-coagulated ink thus removed is collected and recirculated back to the aforesaid ink discharge unit.

[0043] The optical density of the dots of coagulated ink may be varied by varying the voltage and/or pulse duration of the pulse-modulated signals applied to the negative electrodes.

[0044] According to a preferred embodiment, as shown in Fig. 2, step (d-1) is preferably carried out by providing at each transfer position a pressure roller 13 extending parallel to the positive cylindrical electrode 3 and pressed thereagainst to form a nip 14 and permit the pressure roller 13 to be driven by the positive electrode 3 upon rotation thereof, and passing the substrate S through the nip 14. Preferably, the pressure roller is provided with a peripheral covering of a synthetic rubber material such as a polyurethane having a Shore A hardness of about 95. A polyurethane covering with such a hardness has been found to further improve transfer of the coagulated ink from the positive electrode surface onto the substrate. The pressure exerted between the positive electrode and the pressure roller preferably ranges from about 50 to about 100 kg/cm^2.

[0045] After step (d-1), the positive electrode surface is generally cleaned to remove therefrom any remaining coagulated ink. According to a preferred embodiment, as shown in Fig. 2, the positive electrode is rotatable in a predetermined direction and any remaining coagulated ink is removed from the positive electrode surface by providing an

elongated rotatable brush 151 extending parallel to the longitudinal axis of the positive electrode 3, the brush being provided with a plurality of radially extending bristles 152 made of horsehair and having extremities contacting the positive electrode surface, rotating the brush 151 in a direction opposite to the direction of rotation of the positive electrode 3 so as to cause the bristles 152 to frictionally engage the positive electrode surface, and directing jets of cleaning liquid produced by high pressure injectors 153 under pressure against the positive electrode surface. In such an embodiment, the positive electrode surface and the ink are preferably maintained at a temperature of about 35-60°C by heating the cleaning liquid to thereby heat the positive electrode surface upon contacting same and applying the ink on the heated electrode surface to cause a transfer of heat therefrom to the ink.

[0046] Figure 3 shows a schematic illustration of a multicolor electrocoagulation printing apparatus for carrying out the method of the present invention. This apparatus 2 comprises a central positive electrode 3 in the form of a revolving cylinder and four identical printing units 20 (20A, 20B, 20C, 20D) arranged around the positive cylindrical electrode 3, wherein the first printing unit 20A is adopted to print in yellow color, the second printing unit 20B in magenta color, the third printing unit 20C in cyan color and the forth printing unit 20D in black color, respectively.

[0047] In a particularly preferred embodiment, there are at least two printing stages each including one such pressure roller 131 and wherein the pressure rollers are arranged in pairs with the pressure rollers of each pair being diametrically opposed to one another. The provision of two pairs of diametrically opposed pressure rollers arranged around the positive cylindrical electrode 3 prevents such an electrode from flexing since the forces exerted by the pressure rollers of each pair cancel each other out.

[0048] An endless non-extendible belt 17 moving at substantially the same speed as the positive electrode 3 has on one side thereof a coagulated ink retaining surface 171 and is brought into contact with the positive electrode surface 3 by the pressure rollers 131 to cause transfer of the dots of coagulated ink from the positive electrode surface onto the coagulated ink retaining surface 171.

[0049] Preferably, the dots of the electrocoagulation printing ink representative of the polychromic image are moistened between the aforementioned steps (e) and (f) so that the polychromic image is substantially completely transferred onto the substrate. As shown in Fig. 3, use can be made of a moistening unit 19 comprising a plurality of spray nozzles 191.

[0050] According to another preferred embodiment, the substrate is in the form of a continuous web and step (f) is carried out by providing a support roller 135 and a pressure roller (not shown) extending parallel to the support roller 135 and pressed thereagainst to form a nip through which the belt 17 is passed, the support roller 135 and pressure roller being driven by the belt 17 upon movement thereof. The web S is guided by a pair of guide rollers 137 so as to pass through the nip between the pressure roller and the coagulated ink retaining surface 171 of the belt 17, for being imprinted with the polychromic images 200 which are transferred from the surface 171 onto the web S. Preferably, the belt 17 with the coagulated ink retaining surface 171 thereof imprinted with the polychromic images 200 is guided so as to travel along a path extending in a plane intersecting the longitudinal axis of the positive electrode 3 at right angles, thereby exposing the coagulated ink retaining surface to permit contacting thereof by the web S. Where the longitudinal axis of the positive electrode extends vertically, the belt is preferably guided so as to travel along a horizontal path with the coagulated ink retaining surface facing downwardly, the support roller and pressure roller having rotation axes disposed in a plane extending perpendicular to the horizontal path. Such an arrangement is described in the aforementioned US application filed concurrently with the present application, the teaching of which is incorporated herein by reference.

[0051] After step (f), the coagulated ink retaining surface of the belt is generally cleaned to remove therefrom any remaining coagulated ink. According to a preferred embodiment, as shown in Fig. 3, any remaining coagulated ink is removed from the coagulated ink retaining surface 171 of the belt 17 by providing at least one elongated rotatable brush 211 disposed on the one side of the belt 17 and at least one support roller 213 extending parallel to the brush 211 and disposed on the opposite side of the belt 17, the brush 211 and support roller 213 having rotation axes disposed in a plane extending perpendicular to the belt 17, the brush 211 being provided with a plurality of radially extending bristles 212 made of horsehair and having extremities contacting the coagulated ink retaining surface, rotating the brush 211 in a direction opposite to the direction of movement of the belt 17 so as to cause the bristles 212 to frictionally engage the coagulated ink retaining surface while supporting the belt 17 with the support roller 213, directing jets of cleaning liquid under pressure against the coagulated ink retaining surface 171 by using at least one high pressure injector 215, and removing the cleaning liquid with any dislodged coagulated ink from the coagulated ink retaining surface 171.

[EXAMPLE]

[0052] The present invention will be explained in more detail with reference to the following examples which are not intended to be limiting of the present invention insofar as it may be made without departing from the spirit of the invention.

[Example 1]

[0053] A coating agent comprising 7.5% by weight of Silica FK 500LS (BET surface area: 450 m^2/g) manufactured by Degussa AG as the silicon oxide and 92.5% by weight of oleic acid as the oily substance was produced. The viscosity of the coating agent was 3000 cps (30°C).

[0054] The electrocoagulation printing ink was manufactured from the following raw materials:

- Carbon black pigment (Carbon black Monarch 120: Cabot Corporation)	8.8% by weight
- Aqueous anionic dispersant solution (effective component: 42% by weight) (Closperse 2500: Boehem Filatex Canada Inc.)	0.75% by weight
- Anionic acrylamide polymer (Accostrength 86: Mitsui Cytec, Ltd.)	8.8% by weight
- Potassium chloride (soluble electrolyte)	8.8% by weight
- EDTA disodium dihydrate (metal ion chelating agent)	0.03% by weight
- Water (liquid medium)	72.82% by weight
Total	100% by weight

[0055] The coating agent was used in an electrocoagulation printing apparatus of the type described in U.S. Patent No. 4,895,629. The electrocoagulation printing ink and a cleaning liquid used for cleaning the positive electrode were heated to 40°C, thereby to maintain the ink and the positive electrode surface at 40°C. Printing was intermittently carried out for about 40 hours. When the level of the electrocoagulation printing ink in the ink discharge unit dropped, the ink was added to keep a solution level constant. After about 40 hours of the printing, conditions of the positive electrode surface and of a resulting printed matter were inspected by eyes.

[0056] As a result, no significant abrasion or pitting was observed on the surface of the positive electrode after about 40 hours since the start of the printing. The resulting printed matter had excellent quality without uneven density.

[Example 2]

[0057] A coating agent comprising 7.5% by weight of Silica FK 500LS mentioned above as the silicon oxide and 92.5% by weight of isostearic acid as the oily substance was produced. The viscosity of the coating agent was 3000 cps (30°C). Printing was performed in the same condition and method as in Example 1 except that the above coating agent was used.

[0058] Substantially the same results as in Example 1 were obtained.

[Example 3]

[0059] A coating agent comprising 7.5% by weight of Silica FK 500LS mentioned above as the silicon oxide and 92.5% by weight of methyl oleate as the oily substance was produced. The viscosity of the coating agent was 3000 cps (30°C). Printing was performed in the same condition and method as in Example 1 except that the above coating agent was used.

[0060] Substantially the same results as in Example 1 were obtained.

[Example 4]

[0061] A coating agent comprising 25.0% by weight of SILYSIA 530 (BET surface area: 500 m^2/g) manufactured by Fuji Silysia Chemical Ltd. as the silicon oxide and 75.0% by weight of oleic acid as the oily substance was produced. The viscosity of the coating agent was 3000 cps (30°C). Printing was performed in the same condition and method as in Example 1 except that the above coating agent was used.

[0062] Substantially the same results as in Example 1 were obtained.

[Example 5]

[0063] A coating agent comprising 7.5% by weight of AEROSIL R972 (BET surface area: 110 m^2/g) manufactured by

Degussa AG as the silicon oxide and 92.5% by weight of oleic acid as the oily substance was produced. The viscosity of the coating agent was 500 cps (30°C). Printing was performed in the same condition and method as in Example 1 except that the above coating agent was used.

[0064] Substantially the same results as in Example 1 were obtained.

[Example 6]

[0065] A coating agent comprising 7.5% by weight of Silica FK 500LS mentioned above as the silicon oxide, 65% by weight of oleic acid as the oily substance, and further 26% by weight of polyoxyethylenetetraoleic acid sorbitol (the number of ethylene oxide addition mols: 30, HLB: 10.5), and 1.5% by weight of ethyl cellulose having a molecular weight of 80,000 was produced. The viscosity of the coating agent was 6000 cps (30°C). Printing was performed in the same condition and method as in Example 1 except that the above coating agent was used.

[0066] Substantially the same results as in Example 1 were obtained.

[Comparative Example 1]

[0067] A coating agent comprising 50% by weight of dichromium trioxide and 50% by weight of oleic acid was produced. The viscosity of the coating agent was 750 cps (30°C). Printing was performed in the same condition and method as in Example 1 except that the above coating agent was used.

[0068] Crater-like pitting with a diameter of from about 1 to about 2 mm was observed on the surface of the positive electrode after the printing was completed. Image density of the portion corresponding to the pitting on the surface of the positive electrode was reduced, providing printing matter with uneven density.

Claims

1. An electrocoagulation printing method comprising the steps of:

   a) providing a positive electrode having a passivated surface moving at substantially constant speed along a predetermined path;

   b) coating the positive electrode surface with a coating agent containing silicon oxide and an oily substance to form on the surface micro-droplets of the coating agent;

   c) forming on the positive electrode surface having micro-droplets thereon a plurality of dots of coagulated ink representative of a desired image, by electrocoagulation of an electrolytically coagulable printing ink comprising an electrolytically coagulable polymer, a liquid medium, a soluble electrolyte and a coloring agent; and

   d-1) bringing a substrate into contact with the positive electrode surface to cause transfer of the dots of coagulated ink from the positive electrode surface onto the substrate and thereby imprint the substrate with the image.

2. A method as claimed in claim 1, wherein steps (b), (c) and (d-1) are repeated several times to define a corresponding number of printing stages arranged at predetermined locations along the path and each using a coloring agent of different color, and to thereby produce several differently colored images of coagulated ink which are transferred at respective transfer positions onto the substrate in superimposed relation to provide a polychromic image.

3. A method as claimed in claim 1, wherein steps (a), (b) (c) and (d-1) are repeated several times to define a corresponding number of printing stages each using a coloring agent of different color and to thereby produce several differently colored images of coagulated ink which are transferred at respective transfer positions onto the substrate in superimposed relation to provide a polychromic image.

4. An electrocoagulation printing method comprising the steps of:

   a) providing a positive electrode having a passivated surface moving at substantially constant speed along a predetermined path;

   b) coating the positive electrode surface with a coating agent containing silicon oxide and an oily substance to form on the surface micro-droplets of the coating agent;

c) forming on the positive electrode surface having micro-droplets thereon a plurality of dots of coagulated ink representative of a desired image, by electrocoagulation of an electrolytically coagulable printing ink comprising an electrolytically coagulable polymer, a liquid medium, a soluble electrolyte and a coloring agent;

d-2) bringing an endless non-extendible belt moving at substantially the same speed as the positive electrode and having on one side thereof a coagulated ink retaining surface adapted to releasably retain dots of electrocoagulated ink, into contact with the positive electrode surface to cause transfer of the dots of coagulated ink from the positive electrode surface onto the coagulated ink retaining surface of the belt and to thereby imprint the coagulated ink retaining surface with the image;

e) repeating steps (b), (c) and (d-2) several times to define a corresponding number of printing stages arranged at predetermined locations along the path and each using a coloring agent of different color, and to thereby produce several differently colored images of coagulated ink which are transferred at respective transfer positions onto the coagulated ink retaining surface in superimposed relation to provide a polychromic image; and

f) bringing a substrate into contact with the coagulated ink retaining surface of the belt to cause transfer of the polychromic image from the coagulated ink retaining surface onto the substrate and to thereby imprint the substrate with the polychromic image.

5. A method as claimed in claims 1 to 4, wherein step (b) is carried out by providing a distribution roller extending parallel to the positive electrode and having a peripheral coating comprising an oxide ceramic material, applying the coating agent onto the ceramic coating to form on a surface thereof a film of the coating agent uniformly covering the surface of the ceramic coating, the film of the coating agent breaking down into micro-droplets having substantially uniform size and distribution, and transferring the micro-droplets from the ceramic coating onto the positive electrode surface.

6. A method as claimed in claims 1 to 5, wherein the silicon oxide in the coating agent is silicon dioxide which is present in the coating agent in an amount of from 2 to 40% by weight, based on the total weight of the coating agent.

7. A coating agent to be used in coating a positive electrode surface in advance of forming on the positive electrode surface a plurality of dots of coagulated ink by electrocoagulation of an electrolytically coagulable printing ink, the coating agent containing silicon oxide and an oily substance.

8. A coating agent as claimed in claim 8, wherein the silicon oxide is silicon dioxide.

9. A coating agent as claimed in claim 8, wherein the silicon dioxide is present in the coating agent in an amount of from 2 to 40% by weight, based on the total weight of the coating agent.

10. A coating agent as claimed in claim 8 or 9, wherein the silicon dioxide has a BET surface area of from 100 to 600 m^2/g.

11. A coating agent as claimed in claims 7 to 10, wherein the oily substance is an olefinic compound which is unsaturated fatty acid selected from the group consisting of arachidonic acid, linoleicacid, linolenic acid, oleic acid and palmitoleic acid.

FIG. 1

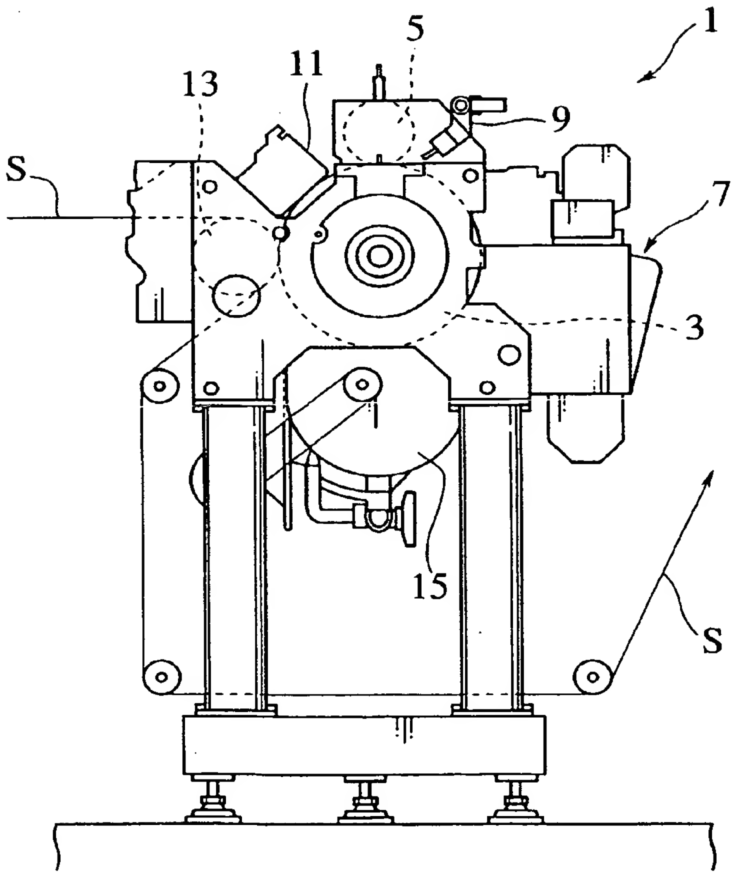
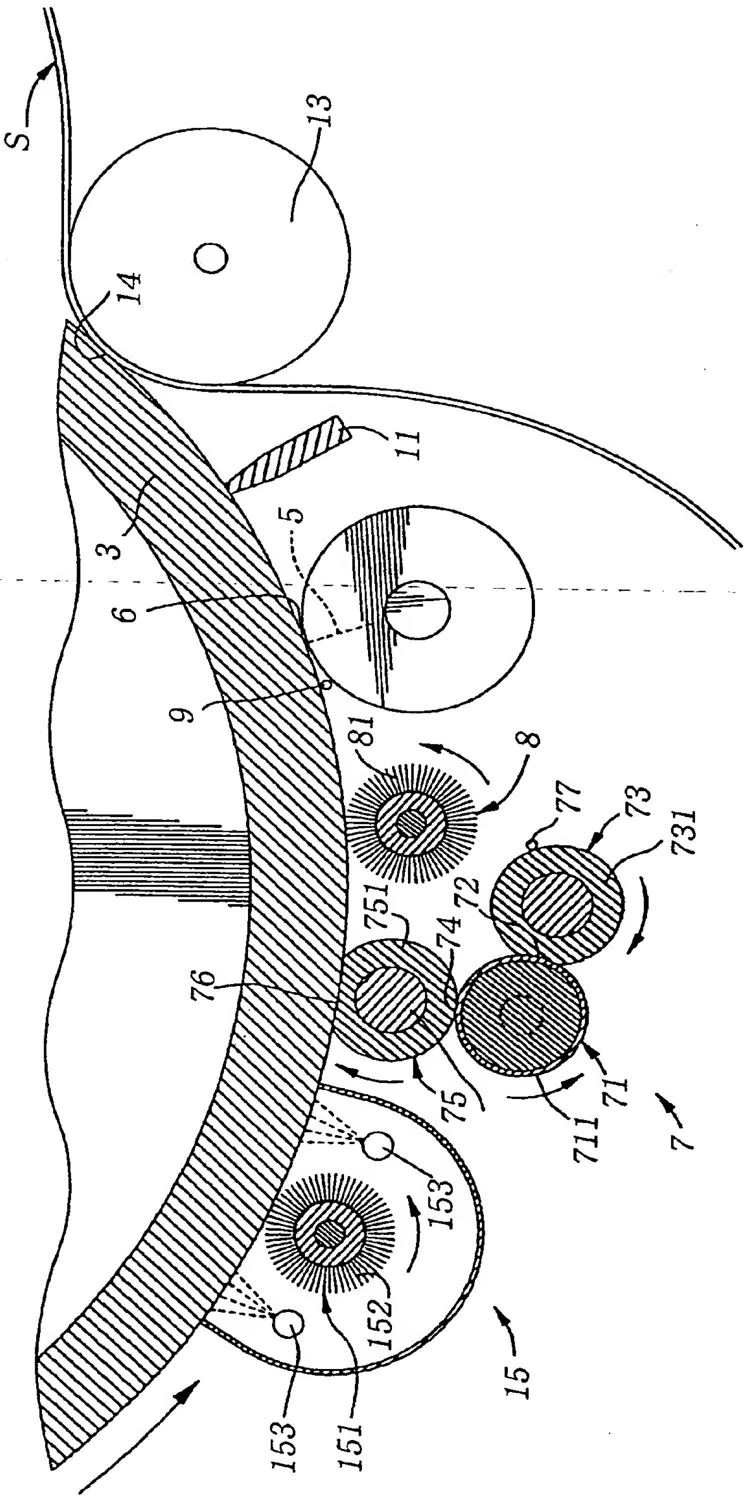


FIG.2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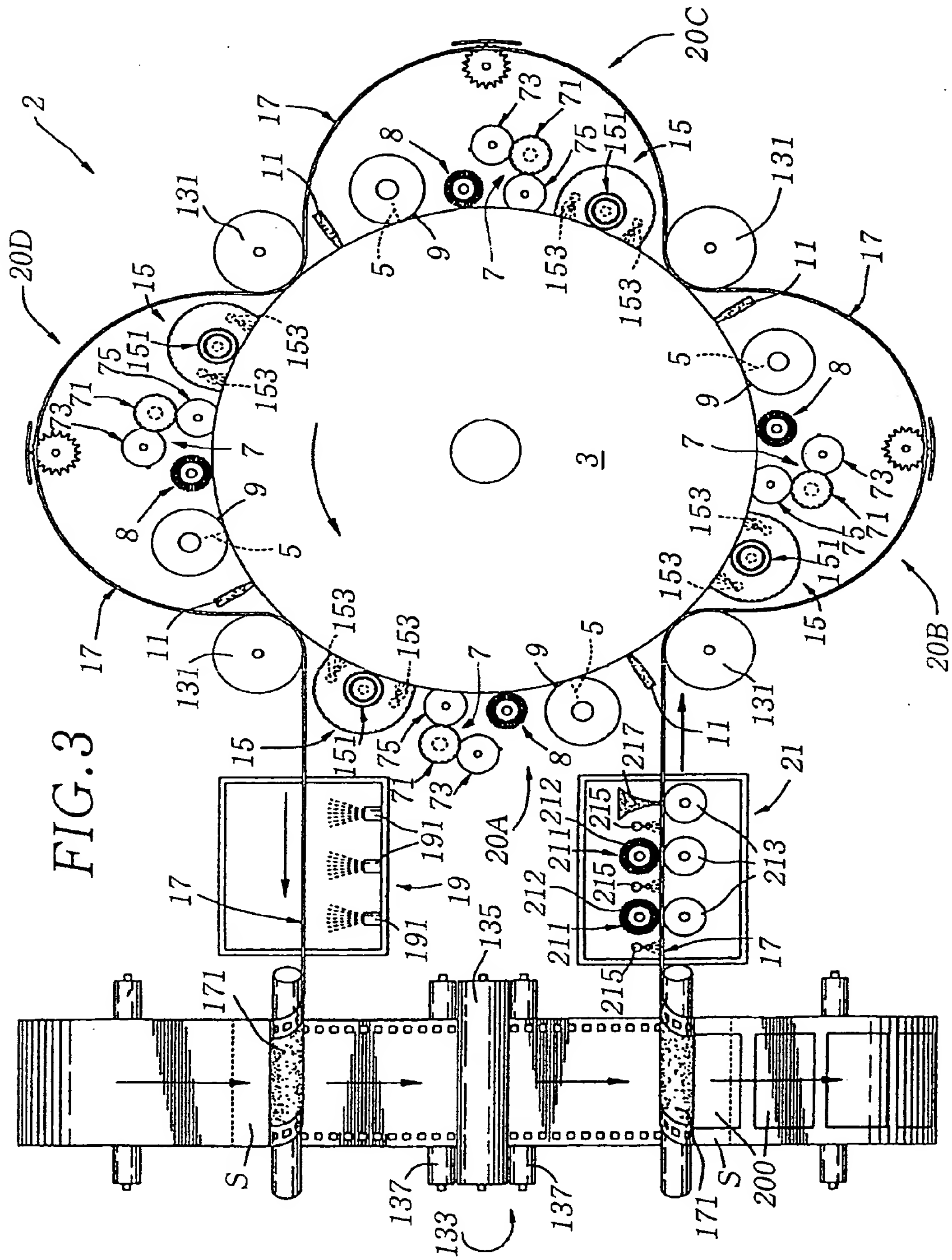

FIG. 3